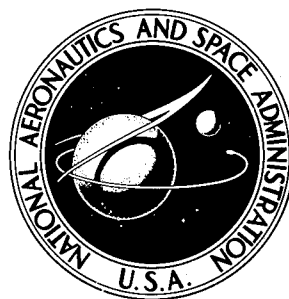


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PREPARATION AND PROPERTIES
OF POLYTETRAFLUOROETHYLENE
IMPREGNATED WITH RHENIUM OXIDES

by Harold F. Leibecki and Robert W. Easter

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16. Abstract <p>The results of tests carried out to determine the properties of polytetrafluoroethylene (PTFE) impregnated with rhenium oxides are presented. The tests included measurement of physical properties of the impregnated material and investigation of the effects of preparation process variables. Based on the latter tests a mechanism to describe the permeation process is postulated which identifies the rate controlling step to be diffusion of ReF_6 molecules into the solid during the initial ReF_6 soak. Physical property tests indicated that the electronic conductance is increased by many orders of magnitude while the desirable properties of the PTFE remain virtually unchanged.</p>					
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PREPARATION AND PROPERTIES OF POLYTETRAFLUOROETHYLENE IMPREGNATED WITH RHENIUM OXIDES

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SUMMARY

It has been observed that polytetrafluoroethylene (PTFE) can be impregnated with rhenium compounds. Studies were made to (1) elucidate the impregnation process, (2) investigate the properties of the impregnated material, and (3) determine if other polyfluorocarbons can be similarly impregnated.

The depth of penetration of the rhenium compounds into the PTFE is proportional to the square root of the rhenium hexafluoride (ReF_6) soak time and is independent of the hydrolysis step in which the ReF_6 is converted to rhenium oxides.

Impregnation leads to an electronic conductance of the order of 10 mhos for a partially impregnated 1- by 1- by 1-centimeter cube while having little or no deleterious effect on the mechanical properties of the sample. Although impregnation leads to an increase of many orders of magnitude in electronic conductivity, the thermal conductivity is essentially unchanged.

It was found that tetrafluoroethylene hexafluoropropylene and polychlorotrifluoroethylene could be impregnated as readily as PTFE, but polyvinylidene fluoride considerably less readily.

INTRODUCTION

It has been found that polytetrafluoroethylene (PTFE) may be soaked in rhenium hexafluoride (ReF_6) and subsequently hydrolyzed to yield materials which are electrically conducting but which retain many of the desirable properties of unimpregnated PTFE (ref. 1). This earlier work indicated that the hydrolysis products remaining in the PTFE were mixed oxides of the metallic constituent of the fluoride used for impregnation.

The present work describes the results of studies undertaken with three objectives in mind: (1) to formulate a plausible model for the permeation process, (2) to investigate

the properties of PTFE permeated with ReF_6 and subsequently hydrolyzed, and (3) to determine if it is possible to permeate polyfluorocarbon materials other than PTFE, namely, tetrafluoroethylene hexafluoropropylene (FEP), polychlorotrifluoroethylene, and vinylidene fluoride.

EXPERIMENT

Table I gives details regarding the samples used. Listed are the sample identifying number, the substrate material, the sample configuration, the ReF_6 soak time, and the tests performed on each sample.

Materials

Commercially available ReF_6 of 99 percent purity was used without further purification in the impregnation step for all samples.

All PTFE samples excepting those for the tensile strength specimens were machined from commercial bulk PTFE prior to impregnation. The tensile strength samples were machined from PTFE meeting military specification MIL P-22296.

The polychlorotrifluoroethylene, FEP, and polyvinylidene fluoride samples were cut or machined from commercial grade materials.

Impregnation and Hydrolysis

The apparatus and procedures used in the soak and hydrolysis steps were identical to those described in reference 1. Unless otherwise noted, the soak was carried out in liquid ReF_6 under its own vapor pressure at ambient temperature, and the samples soaked in ReF_6 were hydrolyzed in water at 373 K for 18 hours. The samples were wiped dry and left in air for 18 hours to dry. Several samples were dried under vacuum (10^{-5} torr) for 18 hours with no observable weight change.

Test Procedures

Test a, weight gain. - The total weight gain of the sample was calculated by difference from weighings before ReF_6 soaking and after hydrolysis and drying.

Test b, penetration distance. - Samples were bisected and standard microscopic, metallographic techniques were used to measure the distance from the sample surface to

the point of abrupt color change. (It was found that the point of brown to white color change is identical with the maximum depth of rhenium oxide penetration as measured by the methods described below.)

Test c, chemical analysis of slices. - The colored layer was removed by machining from all but two opposing faces of a cube sample. These faces were then sliced with a microtome and the slices analyzed individually for rhenium. The slices were between 20 and 50 micrometers in thickness. Analyzable slices at, and immediately behind, the sample surface could not be obtained because of surface roughness; that is, surface slices were fragmentary and tended to crumble to a degree that analysis was judged to be unjustified.

Test d, spectroscopic analysis of slices. - The sample was sliced as in test c, and selected slices were then analyzed for relative rhenium concentration by measuring infrared adsorption at the rhenium-oxygen band, 11.5 micrometers.

Test e, successive hydrolysis. - To determine whether or not the depth of penetration was dependent upon hydrolysis duration, a rod sample was soaked for 72 hours, then subjected to hydrolysis for 1 hour. The rod was then sliced and the penetration depth determined. Hydrolysis was continued, with periodic further slicing and determination of penetration depth, for 18 hours.

Test f, successive rhenium hexafluoride soaks. - Two cube samples were soaked for 72 hours and hydrolyzed. One of the cubes was then given a further ReF_6 soak for 72 hours and hydrolyzed. The total weight gain, penetration depth, and conductivity (see the section Test k, electrical conductivity) were then measured for each cube.

Test g, vapor as opposed to liquid soak. - Two cube samples were soaked simultaneously, one immersed in the liquid ReF_6 and one suspended above the liquid. After 96 hours, the cubes were removed and hydrolyzed and the weight gains and penetration depths were measured.

Test h, tensile strength. - The tensile strength and percent elongation were measured by using ASTM method D 638-68. The samples, which were of Type IV in that method, were soaked for varying times, hydrolyzed, and weighed prior to tensile testing. The test apparatus was a Wiedermann-Baldwin tensile tester.

Test i, hardness. - Samples were tested by using a spring loaded durometer, giving "Shore D" hardness values.

Test j, thermal conductivity. - The thermal conductivity of the completely impregnated sample was measured at 313 and 394 K by a contractor using a standard thermconductometer.

Test k, electrical conductivity. - Soaked and hydrolyzed cube samples were coated on opposite faces with vapor-deposited gold, which served as electrical contacts for conductance measurements. Thus, the conductance is that of a cube containing a nonconducting cubic core of unimpregnated material. The measurements were made at a temperature of 247 ± 2 K with an alternating-current transformer-ratio arm bridge at a

frequency of 15 000 hertz. The applied voltage was 60 millivolts, and the bridge accuracy was 0.1 percent.

Test 1, wear rate. - Wear rates were determined by using the standard NACA "pin-on-disk" method (ref. 2). The method involves cryostating the sample at -162°C and measuring the wear rate against a 4000 rpm disk, with the sample bearing a load of 1 kilogram.

Three samples were tested. One was soaked for 72 hours, hydrolyzed, and tested. The second was soaked for 72 hours, hydrolyzed, soaked for another 72 hours, hydrolyzed, and tested. The third underwent three 72-hour soaks and hydrolyses before being tested.

Test m, chemical and electrochemical inertness. - A sample was immersed for 24 hours at 373 K in either concentrated aqueous potassium hydroxide (KOH) solution (40 percent KOH by weight) or concentrated aqueous phosphoric acid (H_3PO_4) (60 percent H_3PO_4 by weight). The samples were removed and checked visually for degradation, and the solutions were analyzed for rhenium. The same tests were also run with the sample potential driven both anodically and cathodically.

A slice of rhenium-containing Teflon with a vaporized gold contact was cemented with conductive adhesive to a platinum holder. All but the front surface of the electrode was coated with epoxy. The sample was electrolyzed against a platinum-counter electrode. A constant current density of 4 microamperes per square centimeter was used in both the anodic and cathodic cases. The electrolyte was concentrated phosphoric acid, and after 24 hours of electrolysis the electrolyte was analyzed spectroscopically for rhenium.

RESULTS AND DISCUSSION

The test results obtained can be separated into three categories: those concerned with elucidating the impregnation process, measurements of physical properties of impregnated PTFE, and attempts to impregnate polyfluorocarbons other than PTFE.

Elucidation of Impregnation Process

The weight gain and penetration depth data obtained on PTFE samples 1 to 5 are given in table II.

A plot of weight gain and penetration depth for the five samples as a function of the square root of the ReF_6 soak time is shown in figure 1.

Of special interest is the fact that all the penetration depth data are well correlated by a straight line drawn through the origin. The weight gain data from samples 1 to 3

and 5 are also well correlated by a similar straight line through the origin, although the sample 4 weight gain falls considerably below that line.

These data suggest that the observed penetration depth and weight gain may be dependent only on ReF_6 soak time and independent of hydrolysis duration once some small duration "threshold" hydrolysis time is reached. This conjecture is borne out by the results of test e, where there was found to be no change in the observable penetration distance from the inspection after 1 hour to termination of hydrolysis after 18 hours.

The implications of this result and of the square-root-of-soak-time correlations will be considered in more detail in the section Proposed Model of Impregnation Process.

Samples 2 to 5 were also subjected to test c, chemical analysis of slices. The results of these analyses are given in figure 2. This figure was constructed as follows. The wet chemical analytical method yielded grams of rhenium per slice. This value was divided by the calculated area per slice to obtain the ordinate value in grams per square centimeter. This value was assigned to a position corresponding to the midpoint of each slice. The distance abscissa thus consists of the distance from the sample surface to the front of the slice plus one-half the slice thickness, and smoothed line segments connect the points.

The data are presented in this manner to minimize the effect of uncertainties present in the slice thickness measurements.

The slice analyses are in excellent agreement with the visual measurements of depth of penetration shown in table II. That is, the abrupt color change does indeed mark the boundary between impregnated and unimpregnated regions.

Figure 2 also shows that the rhenium concentration is relatively constant up to the impregnation boundary and exhibits only a slight decrease from the outermost regions to the impregnation boundary.

Figure 3 shows the results of test d, the spectroscopic analysis. Here again the abrupt impregnation boundary and the slight inward decrease in concentration are evident.

From figures 2 and 3, it appears that the concentration of rhenium at any point behind the impregnation boundary does not depend on soak time. In other words, once the impregnation boundary passes through a region in the material, that region is apparently very nearly saturated with respect to the amount of hydrolysis product to appear in the region subsequently.

Since the results from tests a to e implied that the ReF_6 soak time controlled the final distribution of rhenium in the impregnated material, tests f and g were run to shed additional light on the ReF_6 penetration process.

The results of test f are presented in table III. These results indicate that the second impregnation of sample 9 was equivalent to a first exposure in the sense that (1) the weight gain was equivalent to that of the first impregnation, and (2) the penetration depth was less than or equal to that of the first impregnation. Since figure 2 indicates that a

single exposure tends to saturate the impregnated region, it must be that the hydrolysis leads to substantial desaturation, which "reopens" sites which can thereafter be resaturated.

The results of test g are presented in table IV. Since the characteristics of the two samples after hydrolysis are virtually identical, the ReF_6 penetration process is apparently independent of whether the sample is exposed to liquid or vapor during the ReF_6 soak.

The slice data of figure 2 indicated that the concentration of rhenium in the impregnated region was independent of impregnation time. If this is true, then the mean density of hydrolysis products (weight gain/impregnated volume) should exhibit no dependency on soak time. Table V shows the mean densities for samples 1 to 5.

Although a firm conclusion is impossible with so little data, it would appear that there is no obvious impregnation time dependency in the mean density of hydrolysis products. This shows that the average void volume and density of adsorption sites is constant in a gross analysis from cube to cube. The deviation of sample 4 can be explained by a decrease in adsorption sites which gives a lower weight gain but not a smaller penetration depth.

The mean densities calculated in this manner are not in good agreement with the local densities calculated from the slice analyses, however. Because of this discrepancy, the method by which local densities were calculated is presented here.

The slice data yield grams of Re per unit volume from

$$\frac{\text{g Re}}{\text{cm}^3} = \frac{\text{g Re per slice}}{\text{volume per slice}}$$

and

$$\begin{aligned} \frac{\text{g product}}{\text{unit volume}} &= \frac{\text{g Re}}{\text{unit volume}} \times \frac{\text{g product}}{\text{g Re}} \\ &= \frac{\text{g Re}}{\text{unit volume}} \times \frac{\text{moles product}}{\text{mole Re}} \times \frac{\text{molecular weight product}}{\text{molecular weight Re}} \end{aligned}$$

The hydrolysis products are assumed to be rhenium oxides (ReO_2 and Re_2O_3) (ref. 1). If the product is all ReO_2 ,

$$\frac{\text{g product}}{\text{unit volume}} = \frac{\text{g Re}}{\text{unit volume}} \times 1.17$$

If the product is all Re_2O_3 ,

$$\frac{\text{g product}}{\text{unit volume}} = \frac{\text{g Re}}{\text{unit volume}} \times 1.13$$

Thus, to within 2 percent regardless of the relative amounts of the two oxides,

$$\frac{\text{g product}}{\text{unit volume}} = \frac{\text{g Re}}{\text{unit volume}} \times 1.15$$

Typical results for local density calculations are 0.104 to 0.135 gram per cubic centimeter, only about one-half the average mean density. The reason for this discrepancy is unknown. Several possibilities exist: errors in estimations of slice volume, the presence of nonrhenium-containing hydrolysis products, loss of product during the microtoming, or formation of a dense surface layer of rhenium oxide which went undetected in the slice analysis.

It should be noted that the impregnated samples did not exhibit noticeable swelling during the process. This fact implies that penetration of the PTFE by bulk liquid at any step of the process was absent.

Proposed Model of Impregnation Process

At this point the experimental observations bearing on the mechanism of the impregnation process may be summarized:

- (1) Exposure to ReF_6 and subsequent hydrolysis yield a material impregnated with mixed rhenium oxides.
- (2) There is a sharp boundary between outer impregnated and inner unimpregnated regions.
- (3) The depth of this boundary is proportional to the square root of the time of exposure (t) to ReF_6 .
- (4) The overall weight gain is also proportional to the square root of exposure time.
- (5) The penetration depth is independent of hydrolysis duration.
- (6) The concentration of rhenium oxides is approximately constant throughout the impregnated region and does not depend on the time of exposure to ReF_6 or on hydrolysis time.
- (7) The impregnation process is the same whether samples are exposed to liquid or vapor ReF_6 .
- (8) No swelling of samples is observed at any stage of the process.

(9) A second exposure to ReF_6 and hydrolysis under conditions identical to the first exposure yield a weight gain comparable to the first, but no increase in penetration depth.

The implications of these observations may now be considered.

Observations (7) and (8) imply that the ReF_6 penetrates the sample by a molecular process as opposed to a bulk phase.

If this is the case, the characteristic $t^{1/2}$ behavior (observation (3) and observation (5)) implies that the depth of penetration is controlled by the diffusion of ReF_6 .

This, coupled with observations (1) and (2), implies that the ReF_6 is chemisorbed at sites within the sample so that the rhenium atom is immobilized.

Finally, observations (4), (6), and (9) imply that the chemisorption is fast with respect to the diffusion step and that the chemisorption process tends to saturate all available sites in the impregnated region, although some sites become available again after hydrolysis.

Based on the preceding rationale the following partial explanation of the impregnation process is postulated.

During the soak step, ReF_6 molecules penetrate into the plastic by diffusion (either through micropores or intermolecular voids) until reaching sites at which they react or chemisorb. The nature of the reaction is unknown but may be akin to the dissolution of some fluoroplastics by fluorinated solvents. The rate of the reaction or chemisorption is very fast with respect to the rate of transport into the interior, and once chemisorbed the rhenium atom is immobilized during subsequent steps of the process. This leads to a sharp boundary which moves into the material, beyond which there is no ReF_6 or chemisorbed rhenium and behind which all accessible sites are occupied by rhenium in the chemisorbed state. During the hydrolysis step the water penetrates the plastic more readily than the ReF_6 because of the smaller size of the molecule and hydrolyzes the chemisorbed rhenium to an oxide without disturbing the position in which it was chemisorbed in the soak step.

Expressions for the penetration depth as a function of soak time derived from this mechanism appear to represent adequately the reported penetration depth data.

The diffusive transport is represented by Fick's second law expression,

$$\frac{\partial^2 c}{\partial X^2} = \frac{1}{D} \frac{\partial c}{\partial t}$$

with conditions

$$c(X, 0) = 0$$

$$c[X_f(t), t] = 0$$

$$c(0, t) = C_o$$

where c is the concentration of ReF_6 ; X the distance from the surface; t the time of soak; $X_f(t)$ the penetration distance; D the effective diffusivity, which is assumed constant; and C_o the surface concentration. The equation may be solved by recasting it in terms of the dimensionless quantities θ and η , where

$$\theta = \frac{c}{C_o}$$

and

$$\eta = \frac{X}{\sqrt{Dt}}$$

The equation thus becomes

$$\frac{d^2\theta}{d\eta^2} + \frac{1}{2} \eta \frac{d\theta}{d\eta} = 0$$

the solution of which is found to be

$$\frac{c}{C_o} = 1 - \frac{\text{erf}\left(\frac{X}{\sqrt{4Dt}}\right)}{\text{erf}\left(\frac{X_f(t)}{\sqrt{4Dt}}\right)} \quad (1)$$

This expression gives the concentration of diffusing ReF_6 behind the penetration front.

If the concentration of sorbed rhenium C_R is constant, the overall rate of chemisorption is given by

$$C_R \frac{dV(X_f)}{dt} = -A(X_f)D \left. \frac{\partial c}{\partial X} \right|_{X_f}$$

where $V(X_f)$ is the impregnated volume and $A(X_f)$ the area of the penetration front.

Differentiating equation (1) and substituting the expressions for $V(X_f)$ and $A(X_f)$, namely,

$$V(X_f) = a^3 - (a - 2X_f)^3$$

$$A(X_f) = 6(a - 2X_f)^2$$

where a is the cube dimension, yield

$$\frac{C_R}{DC_o} \frac{dX_f}{dt} = \frac{2e^{-X_f^2/4Dt}}{\sqrt{4D\pi t} \operatorname{erf}\left(\frac{X_f}{\sqrt{4Dt}}\right)}$$

which may be solved to yield

$$X_f = kt^{1/2} \quad (2)$$

with k given (implicitly) by

$$\frac{k}{\sqrt{4D}} e^{(k/\sqrt{4D})^2} \operatorname{erf} \frac{k}{\sqrt{4D}} = \frac{C_o}{\sqrt{\pi C_R}}$$

or if $C_o/\sqrt{\pi C_R}$ is less than 10^{-2} , the approximation $ue^{u^2} \operatorname{erf} u \simeq 1.13 u^2$ may be employed to yield

$$k = \sqrt{2.0 \left(\frac{C_o D}{C_R} \right)} \quad (3)$$

The model thus predicts the $t^{1/2}$ dependency of the penetration depth data and yields an expression for the slope k . Further studies would be necessary to determine the various parameters to see if the result for k is correct.

By this approach the weight gain M as a function of soak time t for cubic samples is given by

$$M(t) = C_R a^3 \left[6 \left(\frac{kt^{1/2}}{a} \right) - 12 \left(\frac{kt^{1/2}}{a} \right)^2 + 8 \left(\frac{kt^{1/2}}{a} \right)^3 \right]$$

This expression indicates that weight gain will be approximately linear with $t^{1/2}$ until $kt^{1/2}/a$ becomes greater than about 0.1, after which the higher order terms begin to have an effect.

Properties of Impregnated Polytetrafluoroethylene

The results of the property tests are qualitatively summarized in table VI, where impregnated samples and unimpregnated samples are compared. Detailed presentation of the test results follows.

The results of the conductance measurements performed on impregnated PTFE are given in table VII. Samples 1, 3 to 5, 8, and 17 are directly comparable, and if sample 4 is omitted, there is an increase of conductance with degree of impregnation. Sample 4 was also noted to have a lower weight gain than the others in the series, and these anomalies might be caused by a decreased void content. Samples 8 and 9 are separate experiments to determine the effect of successive ReF_6 soaks (see the section Test f, successive rhenium hexafluoride soaks). It is not known whether the decreased conductance of sample 9 is a valid result or an erroneous measurement.

The results of the tensile strength tests are given in table VIII. It is apparent that no appreciable change occurs in tensile strength and percent elongation as a result of the impregnation process.

By way of comparison, reported values for other PTFE-base materials are 6.89 to 27.6 meganewtons per square meter (1000 to 4000 lb/in.²) for granular resin PTFE, 8.96 to 18.6 meganewtons per square meter (1300 to 2700 lb/in.²) for 15 percent graphite filled PTFE, and 19.3 to 24.8 meganewtons per square meter (2800 to 3600 lb/in.²) for 15 percent glass-fiber-filled PTFE (ref. 3).

The results of the hardness tests are given in table IX. It appears that there is no significant change in the hardness of the PTFE even with complete impregnation.

The results of the thermal-conductivity test performed on a portion of the completely impregnated tensile-strength sample are given in table X, along with comparative values for untreated PTFE.

The wear-rate test results are given in table XI. These results indicate a threefold decrease in wear rate in the singly impregnated sample. The increased wear rate after successive impregnations may reflect structural weakening due to the postulated solvent attack character of the ReF_6 chemisorption reaction.

The chemical and electrochemical inertness tests indicated that the inherent chemical stability of the PTFE is not affected by the impregnation process and that the hydrolysis product is quite stable. No observable changes took place in the samples as a result of any of the soaks, and no rhenium was detected in any of the soak solutions.

Impregnation of Polyfluorocarbons Other Than Polytetrafluoroethylene

Since the polymerization of tetrafluoroethylene results in particulate PTFE, bulk PTFE must be produced by methods akin to sintering. This leads to a relatively porous bulk material, as compared to other bulk polyfluorocarbons produced by other methods. (The measured specific gravity of samples 1 to 5 was 2.13 as compared to a theoretical perfect crystal specific gravity of 2.30 (ref. 4).) Thus, polychlorotrifluoroethylene, FEP, and polyvinylidene fluoride might be expected to be less readily impregnated than is PTFE.

It was found, however, that only polyvinylidene fluoride was appreciably more resistant to impregnation than PTFE. Both FEP and polychlorotrifluoroethylene behaved in a manner quite similar to PTFE.

The results of the polychlorotrifluoroethylene tests are given in table XII. No conductance value was obtained for sample 27 because the sample was inadvertently destroyed during deposition of the gold contacts. The two remaining measurements indicate that the conductivity decreased, rather than increased, with increasing ReF_6 impregnation time. More data would be required to determine if this is actually the case.

The penetration-depth data exhibit the same $t^{1/2}$ dependency as did the PTFE data, and if plotted in figure 1 would be represented by the same straight line through the origin. The weight gains are consistently higher, however, than those exhibited by PTFE samples having the same soak time.

It would appear from these results that the density of sorption sites within the polychlorotrifluoroethylene is somewhat higher than within the PTFE, as is the effective diffusivity. Further tests would be necessary to determine the dependency of these quantities upon relative crystallinity, degree of fluorination, and other such properties of the different polymers.

CONCLUSIONS

The following conclusions were drawn from a study of the preparation and properties of polytetrafluoroethylene impregnated with rhenium oxides.

Elucidation of Permeation Process

The available data and observations may be correlated by postulating a model in which the controlling step is the penetration of rhenium hexafluoride (ReF_6) during the ReF_6 soak period. The ReF_6 is thought to penetrate by diffusion through intermolecular voids in the plastic.

Although this model adequately explains the existing data, an overall lack of data prevents a firm conclusion as to the validity of the model.

Properties of Polytetrafluoroethylene Impregnated With Rhenium Oxides

Impregnation by rhenium increases the conductance of polytetrafluoroethylene (PTFE) samples by several orders of magnitude and leads to a threefold decrease in wear rate, while leaving the tensile strength, hardness, thermal conductivity, and chemical resistance to acids and bases essentially unchanged.

Impregnation of Polyfluorocarbons Other Than Polytetrafluoroethylene

Contrary to expectation, it was found that the relatively nonporous materials, tetrafluoroethylene hexafluoropropylene and polychlorotrifluoroethylene, became impregnated as readily as PTFE. Only polyvinylidene fluoride was much more resistant to impregnation.

This implies that the impregnation process is not dependent on macroscopic voids for transport into the interior.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, October 30, 1972,
502-25.

REFERENCES

1. Leibecki, Harold: Observations on Permeation of Polytetrafluoroethylene by Compounds of Rhenium, Molybdenum, and Tungsten. NASA TN D-4886, 1968.
2. Wisander, D. W.; Hady, W. F.; and Johnson, R. L.: Friction Studies of Various Materials in Liquid Nitrogen. NACA TN 4211, 1958.
3. Anon.: Teflon Fluorocarbon Resin Mechanical Design Data. Plastics Department, E. I. DuPont De Nemours and Co., Inc., Wilmington, Del.
4. Sperati, C. A.; and Stackweather, H. W., Jr.: Fluorine Containing Polymers: II - Polytetrafluoroethylene. Polychemicals Dept. E. I. DuPont De Nemours and Co., Inc., DuPont Experimental Station, Wilmington, Del.

TABLE I. - SAMPLES AND TESTS

(a) Samples

Sample	Substrate	Configuration	ReF ₆ soak time, hr	Tests
1	PTFE	Cube, 1 cm ³	24	a, b, c, k
2	↓	↓	48	↓
3	↓	↓	72	↓
4	↓	↓	96	↓
5	↓	↓	120	↓
6	↓	↓	120	d
7	PTFE	Rod	72	e
8	PTFE	Cube, 1 cm ³	72	f
9	↓	↓	144	
10	↓	↓	96	g
11	↓	↓	96	
12	PTFE	Tensile-strength specimen	0	a, h, j
13	↓	↓	72	a, h
14	↓	↓	96	a, h
15	↓	↓	120	a, h
16	↓	↓	^a 2952	a, h, i, j
17	PTFE	Cube, 1 cm ³	0	i, k
18	PTFE	Cube, 1 cm ³	24	i
19	PTFE	Cube, 1 cm ³	96	i
20	PTFE	Wear-rate specimen	0	1
21	↓	↓	72	↓
22	↓	↓	72, 72	↓
23	↓	↓	72, 72, 72	↓
24	PTFE	Slab	24	m
25	PTFE	Slab	24	m
26	Polychlorotri-fluoroethylene	Cube, 1 cm ³	24	a, b, k
27	Polychlorotri-fluoroethylene	Cube, 1 cm ³	48	a, b, k
28	Polychlorotri-fluoroethylene	Cube, 1 cm ³	120	a, b, k
29	FEP	Strip	24	-----
30	Polyvinylidene fluoride	Strip	24	-----

(b) Tests

Test	Description
a	Weight gain
b	Penetration distance
c	Chemical analysis of slices
d	Spectroscopic analysis of slices
e	Successive hydrolysis
f	Successive rhenium hexafluoride soaks
g	Vapor as opposed to liquid soak
h	Tensile strength
i	Hardness
j	Thermal conductivity
k	Electrical conductivity
l	Wear rate
m	Chemical and electrochemical inertness

^a123 days.

TABLE II. - WEIGHT GAIN AND PENETRATION DEPTH

PTFE sample	ReF ₆ soak time, hr	Weight gain, mg	Depth of penetration, μm
1	24	57 \pm 0	552 \pm 13
2	48	86 \pm 2	701 \pm 16
3	72	105 \pm 3	960 \pm 25
4	96	89 \pm 4	1050 \pm 16
5	120	129 \pm 1	1160 \pm 33

TABLE III. - COMPARISON OF SINGLY AND
DOUBLY SOAKED AND HYDROLYZED
SAMPLES (TEST f)

PTFE sample	72 hr	144 hr	72 hr	144 hr
	Total weight gain, mg		Penetration, μm	
8	105	---	1030	----
9	105	217	----	1030

TABLE IV. - RHENIUM HEXAFLUORIDE LIQUID EXPOSURE
COMPARED TO VAPOR EXPOSURE (TEST g)

PTFE sample	ReF ₆ soak time, hr	Soak mode	Weight gain, mg	Penetration, μm
10	96	Liquid	80.5	1030
11	96	Vapor	80.1	1030

TABLE V. - MEAN DENSITIES OF SAMPLES 1 TO 5

[Average mean density, 0.211 g/cm^3 ; average deviation, 0.024 g/cm^3 or 11.4 percent; maximum deviation, 0.035 g/cm^3 or 16.6 percent.]

PTFE sample	ReF ₆ soak time, hr	Weight gain, g	Impregnated volume ^a , cm ³	Mean density of impregnated volume, g/cm ³
1	24	0.057	0.28 to 0.31	0.20 to 0.19
2	48	.086	0.35 to 0.38	0.25 to 0.23
3	72	.105	0.46 to 0.48	0.23 to 0.22
4	96	.89	0.50 to 0.51	0.18 to 0.17
5	120	.129	0.53 to 0.55	0.24 to 0.23

^aImpregnated volume was calculated from volume = $1 - (1 - 2l)^3$, where l is the observed penetration depth; cubes were $1 \pm 0.01 \text{ cm}$ on a side.

TABLE VI. - SUMMARY OF PROPERTY TEST RESULTS

Property	Impregnated PTFE as compared to unimpregnated PTFE
Electrical conductance	Increase by factor of 10^{18}
Hardness	No change
Tensile strength and percent elongation	No change
Thermal conductivity	No change
Wear rate	Threefold decrease for 72-hr ReF ₆ soak
Chemical and electro-chemical inertness	No change

TABLE VII. - CONDUCTANCE MEASUREMENTS (TEST k)

PTFE sample	ReF ₆ soak time, hr	Weight gain, mg	Conductance, mhos
17	0	0	10^{-18}
1	24	57	0.96
3	72	105	20.9
4	96	89	2.71
5	120	129	38.4
8	72	105	20.9
9	144	217	.014

TABLE VIII. - TENSILE STRENGTH AND ELONGATION (TEST h)

PTFE sample	ReF ₆ soak time, hr	Weight gain, mg	Tensile strength, MN/m ³	Elongation, percent
12	0	----	26.4	294
13	72	972	25.0	309
14	96	1041	26.0	294
15	120	1058	26.8	319
16	123 days	2313	21.0	294

TABLE IX. - HARDNESS (TEST i)

PTFE sample	ReF ₆ soak time, hr	Approximate total depth of impregnation, percent	Hardness (Shore D)
17	0	0	60
18	24	30	63
19	96	51	63
16	^a 2952	100	55

^a123 days.

TABLE X. - THERMAL CONDUCTIVITY (TEST j)

Sample	ReF ₆ soak time, hr	313 K	394 K
		Thermal conductivity, W/(m)(K)	
Untreated PTFE	0	0.335	0.35
16	^a 2952	.345	.365

^a123 days.

TABLE XI. - WEAR RATE (TEST l)

PTFE sample	ReF ₆ soak time, hr	Wear rate, cm ³ /hr
^a 20	0	6.2×10 ⁻²
21	72	2.0
22	72+72	4.4
23	72+72+72	4.6

^aUntreated.

TABLE XII. - IMPREGNATION OF POLYCHLOROTRIFLUOROETHYLENE

Sample	ReF ₆ soak time, hr	Weight gain, mg	Penetration depth, μm	Conductance, mhos
26	24	82	534	30.3
27	48	104	864	-----
28	120	201	1170	5.01

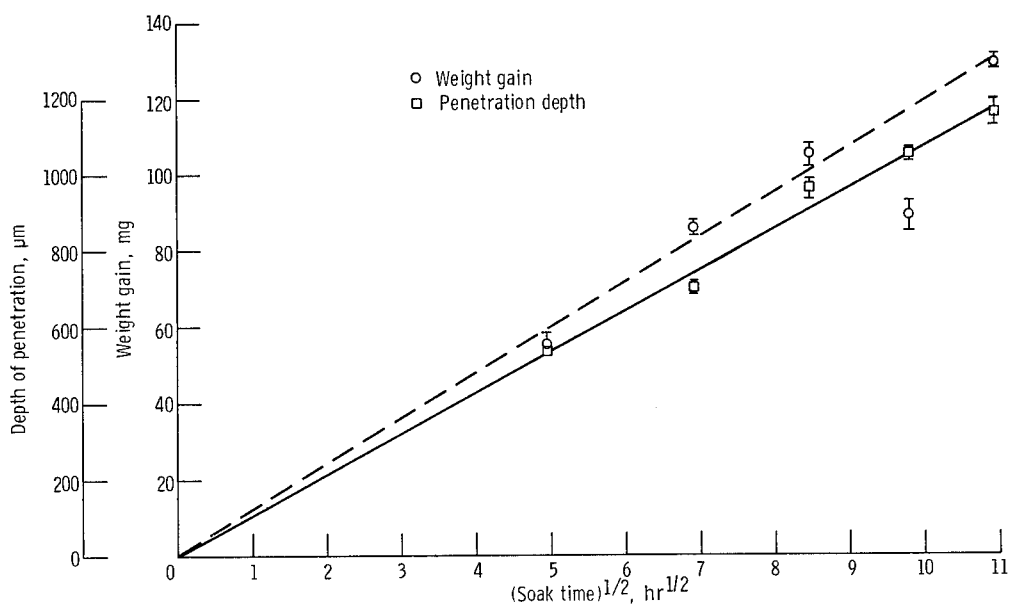


Figure 1. - Weight gain and depth of penetration as function of square root of rhenium fluoride soak time for samples 1 to 5. Slope of penetration depth line, 1.79×10^{-4} centimeter per second^{1/2}.

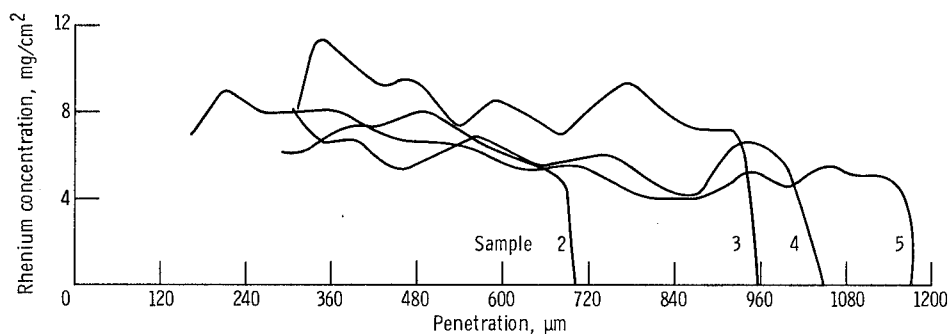


Figure 2. - Concentration profile for rhenium oxide in polytetrafluoroethylene.

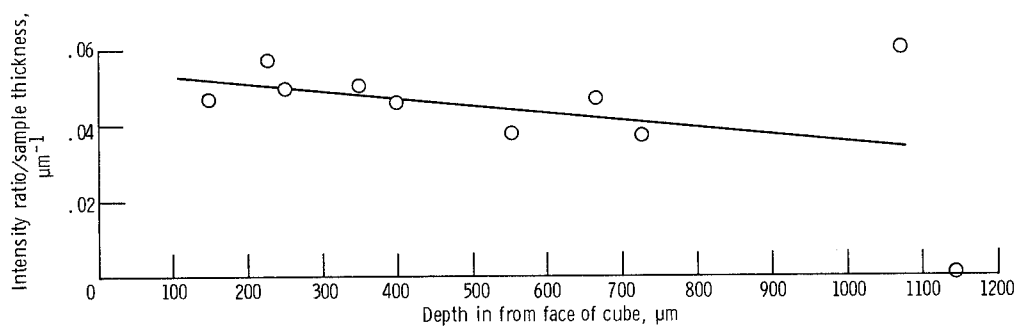


Figure 3. - Spectroscopic rhenium concentration as function of distance from surface.

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